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Spectroscopic Analysis of NIR-Dye Sensitization in Bulk Heterojunction Polymer Solar Cells

Shinzaburo Ito, Hideo Ohkita, Hiroaki Bente, Satoshi Honda

Abstract

The photovoltaic conversion efficiency for near infrared (NIR) sunlight is improved successfully by dye sensitization of bulk heterojunction polymer solar cells, in which the active layer was prepared by a ternary blend of poly(3-hexylthiophene) (P3HT), a fullerene derivative (PCBM), and an NIR dye, silicon phthalocyanine (SiPc). The mechanism of the NIR-dye sensitization is studied by femtosecond transient absorption spectroscopy.

Keywords Polymer solar cell / Near-infrared dye / Transient absorption spectroscopy / Bulk heterojunction / Photovoltaic conversion efficiency

Introduction

The development of science and technology to utilize abundant renewable energy is expected to allow a reduction in the current huge amount of consumption of fossil fuels, and to supply sustainable energy while preserving clean environment of the earth. One promising candidate is polymer solar cells that convert solar energy directly into electricity. Bulk heterojunction (BHJ) solar cells – fabricated by spin-coating of a blend solution of a conjugated polymer and a fullerene derivative – have attracted much interest since the conversion efficiency has continuously increased. The present best value is 8.3% (Green et al. 2011) and will reach 10% in the near future. To achieve further improvement, it is critical for polymer solar cells to increase the conversion efficiency for near infrared (NIR) sunlight in the wavelength range of 700–900 nm. Therefore many synthetic studies have been done to explore new low-bandgap polymers having strong absorption bands in the NIR region. Recently, we have proposed a novel strategy: dye sensitization of bulk heterojunction polymer solar cells, in which the active layer was prepared by a ternary blend of poly(3-hexylthiophene) (P3HT), a fullerene derivative (PCBM), and an NIR dye, silicon phthalocyanine (SiPc) (Honda et al. 2009, 2010). Owing to the large absorption coefficient of dye molecules, the NIR light can be collected in the solar cell as well as the visible light.

Results and discussion

The samples were prepared by a ternary blend of regioregular poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM), silicon phthalocyanine bis(trihexylsilyl oxide) (SiPc). About 100 nm thick active layer (P3HT/PCBM/SiPc = 1.0/1.0/0.07 w/w) was spin-coated on an ITO electrode covered with poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS). On the top of the blend film, aluminium was deposited as a counter electrode, and then the whole film was annealed at 150°C for 30 min. The short circuit current density J_{SC} and external quantum efficiency EQE increased compared with the control cells of binary blend (P3HT/PCBM). The large increase in EQE was found not only at the wavelength of SiPc absorption band at 680 nm, but also at the wavelength of P3HT absorption bands around 500 to 600 nm. The former increase is due to direct light absorption by dye molecules, but the latter suggests the presence

of indirect sensitization, mediated through the P3HT absorption. From these results, we propose three mechanisms for sensitization;

- 1) Direct excitation of dyes, followed by charge separation at the interface between P3HT and PCBM domains.
- 2) Excitation of dye molecules through long-range energy transfer from diffusing exciton of P3HT.
- 3) Non-diffusive vectorial energy transfer from P3HT excitons generated at distances shorter than the critical radius from the dye molecule.

In addition, it is also safely concluded that the SiPc dyes are preferentially introduced at the interface between P3HT and PCBM domains as shown in Fig. 1, and effectively contributed to the photocurrent generation.

The light-harvesting mechanism was also studied by femtosecond transient absorption spectroscopy (TAS) with pulsed laser excitation both at the P3HT (400 nm) and SiPc (680 nm) absorption bands (Honda et al. 2011; Ohkita and Ito 2011). Figure 2 shows an example of TAS measurements upon dye excitation of the ternary blends at 680 nm (Fig.2a), and the template spectra for P3HT polaron (dashed-dotted line), SiPc anion (solid line) and PCBM anion (broken line) determined by separate experiments (Fig. 2b). As shown in Fig. 2a, at the beginning immediately after the laser pulse, the spectrum consisted of the broad absorption spectrum of SiPc exciton (0 ps), and then within a few picoseconds, it was quickly changed to the sum of P3HT polaron and SiPc anion spectra (2 ps and 10 ps in Fig.2a). The insert depicts the time dependence of the optical density (DOD) at 900 nm, representing kinetics of P3HT polaron. A clear rise appeared with a time constant of 2 ps indicates the fast hole transfer from the excited SiPc to P3HT, yielding P3HT polaron and SiPc anion. However, the spectrum gradually shifted to longer wavelengths with time, and finally turned to the sum of two component spectra of P3HT polaron and PCBM anion (thick solid line in Fig. 2a). This behavior resulted from charge (electron) shift from SiPc anion to PCBM with a time constant of 50 ps, while keeping the

constant yield of P3HT polaron. These results again indicate that SiPc molecules are preferentially introduced in the disordered P3HT domains formed at the P3HT/PCBM interface.

Upon polymer excitation at 400 nm, P3HT excitons decay more rapidly in ternary blends than in binary blends, suggesting efficient energy transfer from P3HT to SiPc. Once the SiPc exciton is produced through energy transfer from P3HT, the following processes should be the same as the processes mentioned above for dye excitation. Figure 3 summarizes the whole kinetics of this dye sensitization system. The conversion processes start from the excited state of dye molecules, partly generated by the photoexcitation of SiPc, partly by the energy transfer from P3HT. From the decay analysis of P3HT exciton, the rate of energy transfer was found to occur very fast about 4 ps. All these photovoltaic processes are much faster than the deactivation to the ground state. For example, the rates of energy transfer and hole transfer processes are 100 times faster than the intrinsic lifetimes of P3HT and SiPc excitons. Therefore highly efficient quantum yield around unity is achieved in each step of the conversion process. These results clearly indicate that the dye sensitization is one of effective strategy even for polymer solar cells to catch the near infrared sunlight.

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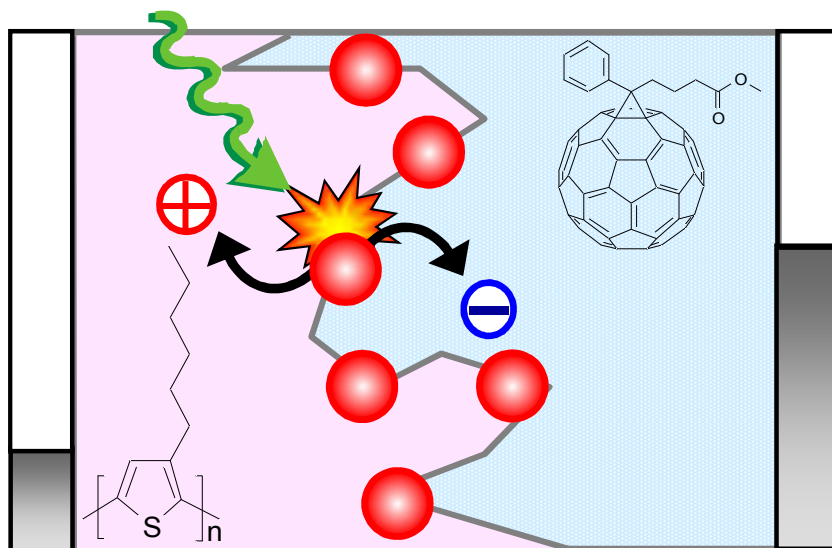


Fig. 1 Schematic drawing of a bulk heterojunction solar cell composed of P3HT/PCBM/SiPc ternary blend, in which SiPcs are selectively placed at the interface of the P3HT/PCBM domains

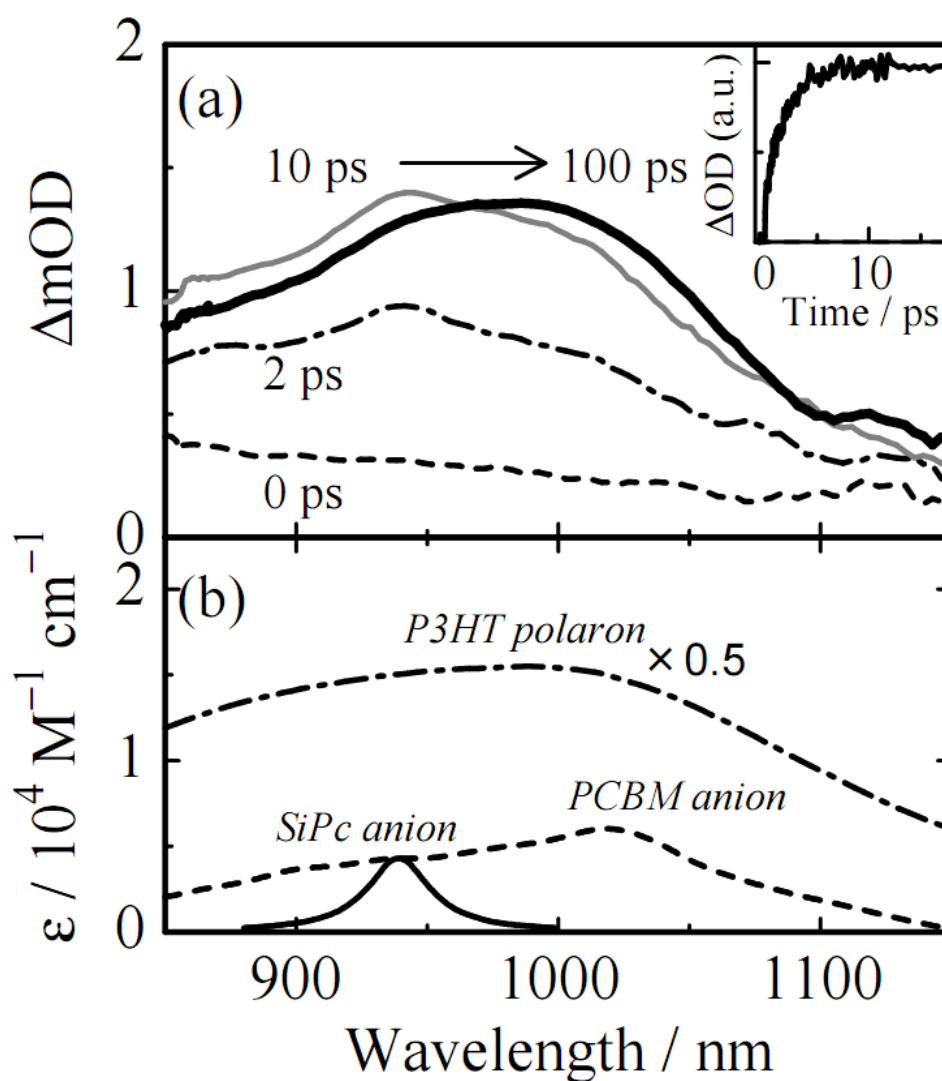


Fig. 2 (a) Transient absorption spectra of P3HT/PCBM/SiPc ternary blend observed with SiPc excitation at 680 nm. Each spectrum was measured at 0 ps (broken line), 2 (dashed-dotted line), 10 ps (solid line), and 100 ps (thick solid line) after the laser excitation. The insert shows the kinetics of P3HT polaron observed at 900 nm.

(b) Molar absorption coefficients (ϵ) of active species: P3HT polaron (dashed-dotted line), PCBM anion (broken line), and SiPc anion (solid line)

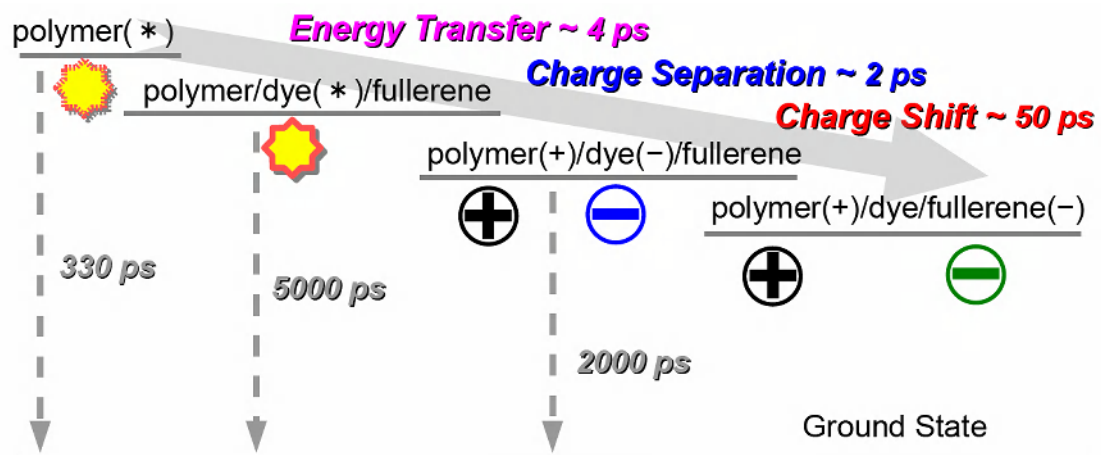


Fig. 3 Summary of dye sensitization processes revealed by TAS analysis